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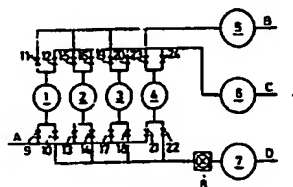
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(54) **Process for producing carbon monoxide gas.**

(57) A process for producing CO gas without using expensive conventional apparatus, in a simple manner in a high purity and with energy saving is provided, which process comprises a step of introducing a by-produced gas such as a mixed gas obtained by reforming or partially oxidizing hydrocarbons, steel converter gas, etc. into a pressure swing adsorption cycle (PSA) system; an adsorption step or adsorbing CO₂, methane, CO, N₂, H₂, etc. in an adsorption column of the PSA system to obtain a H₂-rich gas or a N₂-rich gas passed; a step of depressurizing the adsorption column in the cocurrent direction to obtain a CO-rich gas discharged; a step of depressurizing the adsorption column direction in the counter current direction just prior to start of substantial desorption of methane and CO₂ to obtain a CO₂-rich gas discharged therefrom and having CO₂ and methane concentrated therein; and a step of repressurizing the adsorption column using a H₂-rich gas or a N₂-rich gas obtained at the beginning of the adsorption step and the depressurizing step in the cocurrent direction.

Fig. 1



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Process for producing carbon monoxide gas

This invention relates to a process for producing carbon monoxide (CO) gas used as a basic material for various chemical products such as methanol, acetic acid, phosgen, oxo synthesis products, etc., using hydrocarbon compounds such as natural gas, propane, butane, naphtha, coal, etc. as its raw material.

Heretofore, there have been known a process consisting of reforming hydrocarbon compounds with steam, carbon dioxide (CO₂), etc., removing moisture, removing CO₂ with an absorbing solution such as MEA, etc., liquefying and separating hydrogen from the top of the liquified material and CO from the bottom thereof (Low-temperature separation process), a process consisting of absorbing CO with a solution for selectively absorbing CO such as a toluene solution of CuAlCl₄, heating the solution having absorbed CO and separating and recovering CO (COSORB process), etc.

Since low-temperature separation process requires CO₂ absorber, liquifying means and distilling means, a number of devices and equipments, are necessary and a large quantity of energy is consumed; thus effort for energy saving has been made. As a result, the process has required a complicated heat-exchange system. On the other hand, the COSORB process is a technique monopolized by TENECO Company, LTD. in the U. S. A. and it has drawbacks such as an expensive technical license fee, a deterioration of the absorber, a complicated process for recovering a solvent for the absorber, and further a large quantity of steam for regenerating the absorbing solution. Both the process employ irreversible steps of gas and liquid phase change and gas absorption, as a separation means. Hence, the processes have been commercially unsatisfactory in the aspect of equipments and energy consumption.

In view of the drawbacks of the prior art, an aim of the present invention is to provide a process for producing CO gas capable of separating and recovering it a high concentration, at a small number of steps and in a small quantity of power.

The present invention resides in a process for producing CO gas, comprises the following steps:
 a step of introducing a raw material gas containing carbon dioxide (CO₂), methane (CH₄), carbon monoxide (CO), nitrogen (N₂), and hydrogen (H₂) into a system of pressure swing adsorption cycle;
 a step of adsorbing CO₂, methane, CO, N₂, H₂, etc. in an adsorption column of the system of pressure-swing adsorption cycle to obtain a H₂-rich gas or a N₂-rich gas passed (adsorption step);
 a step of depressurizing the adsorption column in the same current direction as that in the adsorption step to obtain a CO-rich gas desorbed (depressurizing step in the cocurrent direction);
 a step of depressurizing or purging the adsorption column in a current direction counter to that at the adsorption step just prior to start of break through of methane and CO₂ to obtain a CO₂-rich gas discharged therefrom (depressurizing or purging step in the counter current direction); and
 a step of repressurizing the adsorption column using a H₂-rich gas or a N₂-rich gas.

The raw material gas can be a by-produced gas from a steel converter, reformed or partially oxidized hydrocarbons, etc.

The H₂-rich gas or the N₂-rich gas at the step of repressurizing may be one obtained at the adsorption step or at the beginning of the depressurizing step in the cocurrent direction.

The H₂- or N₂-rich gas obtained in the adsorption step may be utilized for repressurizing another column.

The H₂- or N₂-rich gas obtained at the beginning of the depressurizing step in the cocurrent direction may be utilized for equalizing or purging another column.

The CO-rich gas at the depressurizing step in the cocurrent direction may be obtained by depressurizing the column down to 30-200 torr by means of a vacuum pump.

The purging in the counter current direction may be carried out by purging with H₂- or N₂-rich gas at a normal pressure or at a 30-200 torr by means of a vacuum pump.

Embodiments of the present invention will now be described by way of example only with reference to the accompanying drawings, in which:-

Fig. 1 shows a flow sheet illustrating a representative, four column type, pressure swing adsorption cycle system used in the present invention.

Fig. 2 shows a chart illustrating a flow diagram and pressure conditions in the Example of the present invention.

Fig. 3 shows a chart illustrating a process for obtaining a concentrated CO gas or a CO-rich gas from a synthesis gas according to the present invention.

Fig. 4 shows a chart illustrating a process for obtaining a high purity CO gas from a synthesis gas according to the present invention.

Fig. 5 shows a chart illustrating a process for obtaining a high purity CO gas from a by-produced gas

such as converter gas, according to the present invention.

The present invention will be described in more detail by way of Example, but it should not be construed to be limited thereto.

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Example

Fig. 1 shows of a flow sheet illustrating a system for pressure swing adsorption cycle using four adsorption columns, and the following Table 1 shows a sequence of the respective steps using the system:

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Table 1

Column 1	adsorption	depressurizing in the cocurrent direction	depressurizing or purging in the counter current direction	repressurizing in the counter current direction
Column 2	depressurizing or purging in the counter current direction	repressurizing in the counter current direction	adsorption	depressurizing in the cocurrent direction
Column 3	repressurizing in the counter current direction	adsorption	depressurizing in the cocurrent direction	depressurizing or purging in the counter current direction
Column 4	depressurizing in the cocurrent direction	depressurizing or purging in the counter current direction	repressurizing in the counter current direction	adsorption
Note: The cocurrent direction refers to the same gas current direction as that of raw material gas at the adsorption step, and the counter current direction refers to a gas current direction reverse to that of the raw material gas at the adsorption step.				

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The system of Fig. 1 consists of adsorption columns 1-4, gas storage tanks 5-7 storing the respective component gases, vacuum pump 8, and pipelines and valves 9-24 connecting the respective pipelines. The respective steps of the present invention will be described referring to Fig. 1, particularly, adsorption column 1 as an example.

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(1) Adsorption step

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A raw material gas A (1 to 30 atm at normal temperature) having left a reforming furnace, a cracking furnace, a converter, etc. and having a moisture removed therefrom is introduced into an adsorption column 1 under the original pressure as it has, or pressurized to a suitable value (1-30 atm). In the adsorption column 1, adsorption zones of CO₂, methane, CO, N₂ and H₂ in this order are formed (opened valves: 9 and 11 and closed valves: 10 and 12), and just before CO is contained in exit gas, the step is finished, followed by the next step.

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(2) Depressurizing step in the cocurrent direction

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The gas inside the adsorption column 1 is discharged into a tank 6 under a lower pressure (preferably 1-5 atm) in the same gas current direction as that at the adsorption step (opened valve: 12 and closed valves: 9, 10 and 11). At that time, a CO-rich gas is released from the CO adsorption zone, and recovered

to give a product. Just before methane and CO₂ are contained in the exit gas (or just before these gases exceed a tolerable content), the step is finished, followed by the next step.

The lower the desorbed gas at the depressurizing step in the cocurrent direction, the higher the concentration of CO; hence if the pressure is reduced down to 30-200 torr by means of a vacuum pump, higher purity CO can be obtained. On the other hand, the gas desorbed under a relatively high pressure at the beginning of the step is not made a product gas, but for example, it can be mixed with a H₂-rich gas B or a CO₂-rich gas D. Also it can be utilized for repressurizing of other columns by providing a step of equalizing the pressure to that of other columns.

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(3) Depressurizing or purging step in the counter current direction

The adsorption column is further depressurized to about 30-150 torr, preferably by means of a vacuum pump, in the gas current direction counter to that at the adsorption step (opened valve: 10 and closed valves: 9, 11 and 12). This step may be replaced by a purging step with H₂- and N₂-rich gas under a normal pressure or a reduced pressure, obtained at the adsorption step and the depressurizing step in the cocurrent direction. The exit gas at that time is a CO₂-rich gas D which is rich in CO₂ and CH₄ and contains a certain quantity of CO, N₂ and H₂.

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(4) Repressurizing step in the counter current direction

A portion of a H₂ or N₂-rich gas obtained at the above adsorption step is introduced into the adsorption column which has been depressurized to a definite pressure and from which most of the adsorbed gas has been discharged, in the gas current direction counter to that at the adsorption step, to repressurize the column to the original pressure of the adsorption step (opened valve: 11 and closed valves: 9, 10 and 12). By repeating the above steps in adsorption columns 1 to 4, the process of the present invention is carried out.

In the above Example, the set of valves shown in the figure is a mere example, and in order to achieve a smooth gas current at the respective steps, more complicated sets may, of course, be employed. Further, the sequence of the respective steps also shows the basic example of the present invention, and for example, by adding a pressure-equalizing step thereto, it is possible to reduce the capacity of the gas storage tank. Further, four adsorption columns are used above, but the number of the column is not limited and may be one or more, and it is obvious that the smaller the number of columns, the smaller the number of steps at which continuous operation is carried out.

Next, Fig. 3 shows a flow sheet illustrating a process for obtaining a concentrated CO gas or CO-rich gas from a synthesis gas obtained by a reformer or partially oxidizing furnace, using the pressure swing adsorption cycle (PSA) of the present invention.

Fig. 4 shows a flow sheet illustrating a process of obtaining a CO-rich gas from a similar synthesis gas using PSA of the present invention, followed by further treating the resulting gas by means of CO-PSA (CO pressure swing adsorption cycle) system to obtain a high purity CO gas.

Fig. 5 shows a flow sheet illustrating a process of treating a CO-rich gas obtained by treating a by-produced gas such as converter gas by means of PSA system, further by means of CO-PSA system as shown in Fig. 4 to obtain a high purity CO gas, a N₂-rich gas and a CO₂-rich gas, respectively. CO-PSA system in the processes shown in Fig. 4 and Fig. 5 may be replaced by a conventional CO-purifying apparatus.

Example 1

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Using a four column type PSA system having an adsorber filled therein, and under the conditions shown in Fig. 2, the performance of apparatus by way of sequence of the respective steps, each for 180 seconds was measured. The following results were obtained:

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Table 2

		Raw material gas A	H ₂ -rich gas B	CO-rich gas C	CO ₂ -rich gas D
gas current (N /hr)		184	96	43	45
Composition (vol. %)	CO	38.1	20.8	95.7	20.0
	CO ₂	14.8	0	0.7	60.0
	CH ₄	1.3	0	1.2	4.4
	H ₂	45.8	79.2	2.4	15.6

Example 2

Example 1 repeated except that the current of raw material gas was increased as shown in Table 3. The results shown in Table 3 were obtained.

Table 3

		Raw material gas A	H ₂ -rich gas B	CO-rich gas C	CO ₂ -rich gas D
gas current (N /hr)		293	164	50	79
Composition (vol. %)	CO	15.9	1.1	81.2	5.4
	CO ₂	11.5	0	0.4	42.3
	CH ₄	4.4	0	2.6	14.7
	H ₂	68.2	98.9	15.6	37.7

According to the present invention, by using a simple PSA system, without using an expensive conventional apparatus such as low-temperature separation apparatus, gas-absorbing apparatus, etc. in order to produce CO gas, it is possible to obtain a high purity CO gas along with energy-saving and man power-saving. Further, according to the present invention, it is possible to separate at least three kinds of bases composed mainly of H₂, CO and CO₂; hence the process of the present invention is very favorable in the aspect of utilizing these respective component gases. Further, according to the conventional PSA system, it is possible to separate only one component gas per one equipment; hence the above effectiveness could not be expected.

Claims

1. A process for producing carbon monoxide gas, comprising the following steps:
a step of introducing a raw material gas containing carbon dioxide (CO₂), methane (CH₄), carbon monoxide (CO), nitrogen (N₂) and hydrogen (H₂) into a pressure swing adsorption cycle system;
a step of adsorbing CO₂, methane, CO, N₂ and H₂ in an adsorption column of said system to obtain a H₂-rich gas or a N₂-rich gas passed therefrom (adsorption step);
a step of depressurizing said adsorption column in the same gas current direction as that in said adsorption step to obtain a CO-rich gas discharged therefrom (depressurizing step in the cocurrent direction);
a step of depressurizing or purging the adsorption column in a gas current direction counter to that in said

adsorption step just prior to start of break through of methane and CO₂ to obtain a CO₂-rich gas discharged therefrom (depressurizing or purging step in the counter current direction); and
a step of repressurizing the adsorption column using a H₂-rich gas or a N₂-rich gas (repressurizing step in the counter current direction).

5 2. A process according to claim 1 wherein the H₂-rich gas or the N₂-rich gas at the step of repressurizing is one obtained at the adsorption step or at the beginning of the depressurizing step in the cocurrent direction.

3. A process according to claim 1, wherein said H₂- or N₂-rich gas obtained in the adsorption step is utilized for repressurizing another column.

10 4. A process according to claim 1, wherein said H₂- or N₂-rich gas obtained at the beginning of the depressurizing in the cocurrent direction is utilized for equalizing or purging another column.

5. A process according to claim 1, wherein said CO-rich gas is one obtained by depressurizing said column down to 30-200 torr by means of a vacuum pump.

15 6. A process according to claim 1, wherein said purging in the counter current direction is carried out by purging with H₂- or N₂-rich gas at a normal pressure or at a 30-200 torr by means of a vacuum pump.

7. A process according to claim 1, wherein a high concentration gas of CO₂ and methane obtained at said depressurizing step in the counter current direction is mixed with said raw material gas to enhance CO concentration in the gas.

20 8. A process according to claim 7, wherein said raw material gas is obtained from a reformer, a partially oxidizing furnace of hydrocarbons or a steel converter.

9. A process according to claim 1, wherein said pressure swing adsorption cycle system is combined with a CO pressure swing adsorption cycle system to obtain a high purity CO gas from a CO-rich gas.

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Fig. 1

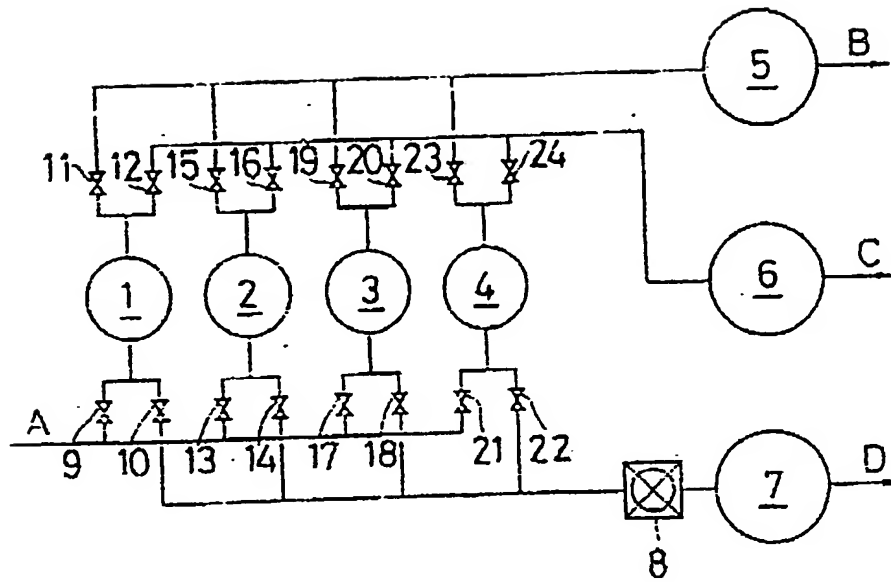


Fig. 2

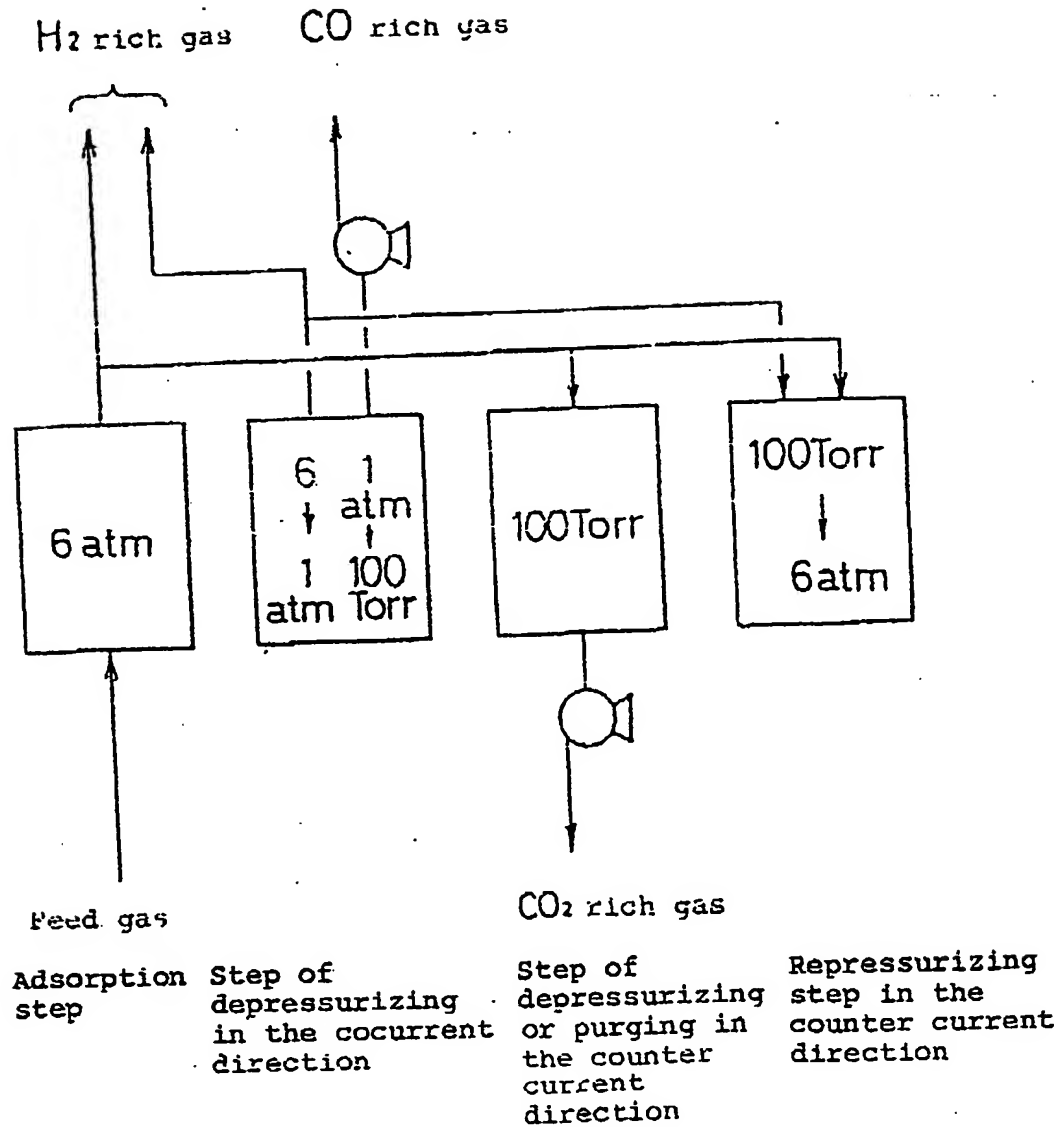


Fig. 3

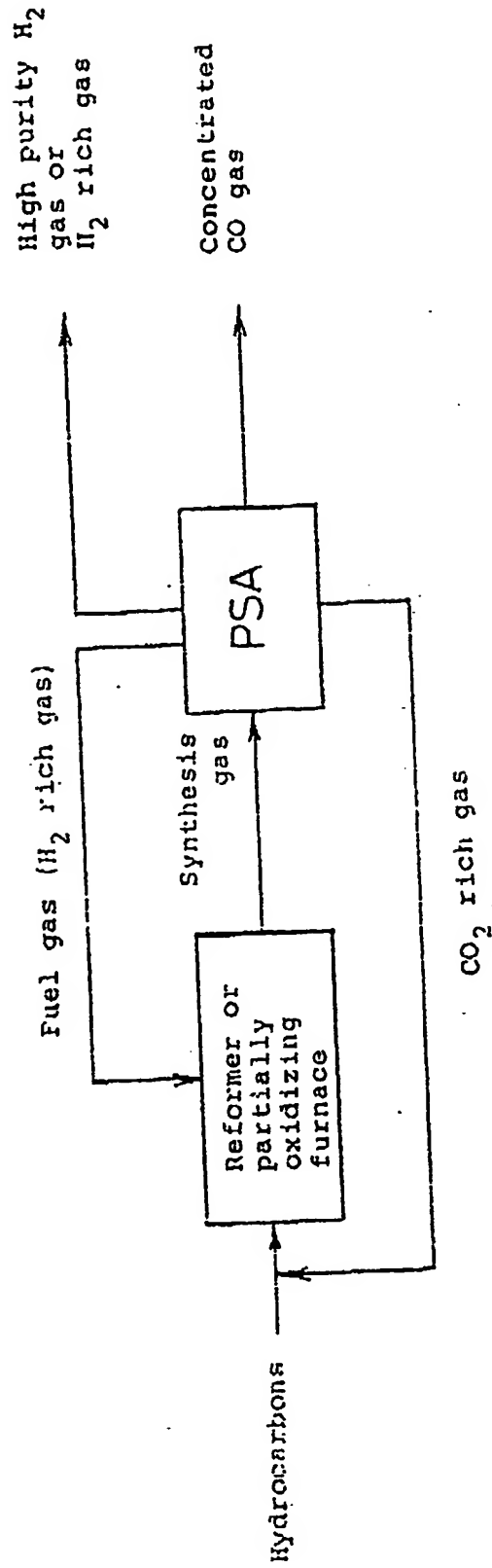


Fig. 4

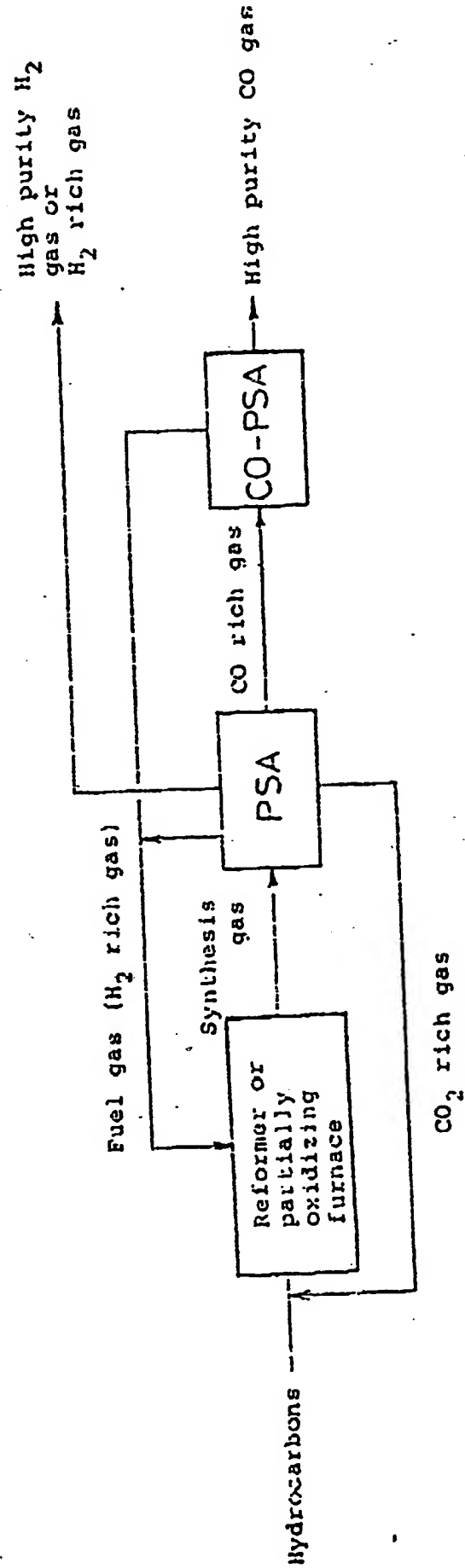
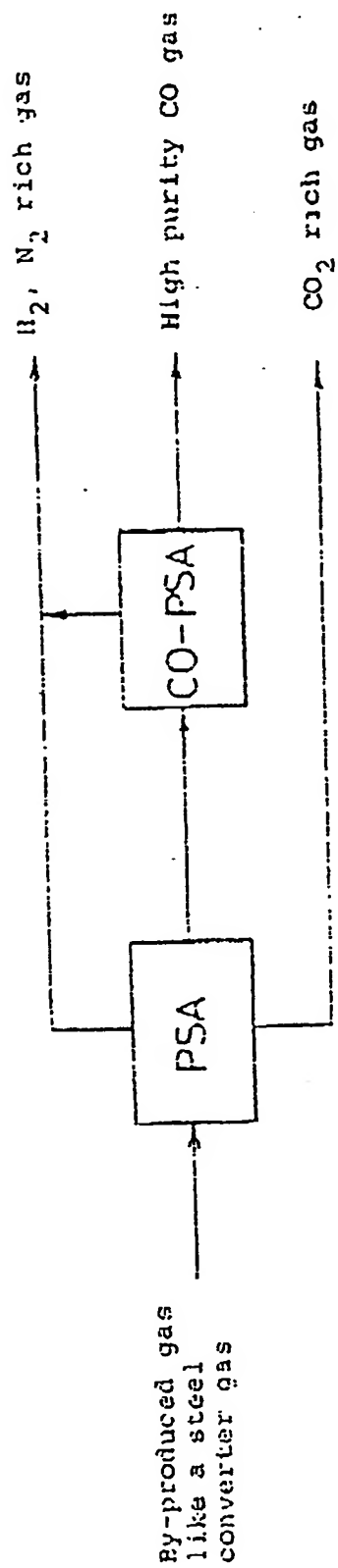


Fig. 5





European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 89 31 1393

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 129 444 (KAWASAKI STEEL) * Claims; figure 5; page 15, line 6 - page 16, line 7 *	1-9	B 01 D 53/04 C 01 B 31/18 C 10 K 1/32
P,A	EP-A-0 314 040 (SAIBU GAS)(03-05-1989) * Figure 1; pages 4,5 *	1,5	
A	EP-A-0 103 070 (BERGWERKSVERBAND)		
A	US-A-4 512 780 (ANDRIJA FUDERER)		
A	US-A-4 723 966 (A. FUDERER)		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			B 01 D C 01 B C 10 K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14-02-1990	Examiner BOGAERTS M. L. M.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	